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## (54) FILTRATION METHOD OF SEPARATING LIQUIDS FROM EXTRANEOUS MATERIALS

(71) We, UNITED STATES ATOMIC ENERGY COMMISSION, Washington, District of Columbia 20545, United States of America, a duly constituted agency of the Government of the United States of America established by the Atomic Energy Act of 1946 (Public Law 585) and the Atomic Energy Act of 1954 (Public Law 703), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to filtration methods of separating liquids from extraneous materials.

Hyperfiltration methods have been developed for removing solute from a solution by dynamically forming a solute-rejecting membrane on a porous substrate and then passing a solution over the resulting substrate under conditions whereby a portion of the liquid is forced through the membrane. Although an excellent solute-rejecting membrane can be formed on a porous substrate, it has been necessary to use a substrate having an average pore diameter of less than 5 microns and preferably having a narrow pore size distribution. Such a substrate is not only difficult to fabricate, but is easily fouled and difficult to clean.

### *Summary of the Invention*

It is accordingly one object of the present invention to provide an improved filtration method of removing extraneous materials from a liquid.

It is another object to provide a hyperfiltration method of removing solute from a solution using a porous substrate having relatively large pores.

It is another object to provide a hyperfiltration medium which is readily cleaned.

We have discovered that a bed of particles uniformly dispersed onto a porous substrate retains its uniformity and functions as a highly efficient filter under cross flow filtration (filtration wherein a liquid being filtered is pumped across the surface of the filtering medium) even at extremely high cross flow rates.

According to the present invention there is provided a process for removing extraneous materials which are dissolved in an aqueous feed solution which comprises depositing to a depth of from 0.1 to 100 microns, a bed of particles of an inert filter aid material on the internal or external surface of a porous tubular substrate, said particles having a size in the range of 0.01 to 100 microns, incorporating a solute-rejecting material in said feed solution if not originally present therein, and passing said feed solution across the deposited bed while maintaining a velocity parallel to the bed sufficient to prevent fouling of the solute-rejecting membrane formed thereon from said solute-rejecting material and a pressure across said bed sufficient to cause an aqueous solution to issue from the non-deposited surface of said substrate which solution is depleted in extraneous materials.

This method is especially useful in separation processes wherein a uniform, finely pored structure is necessary such as in processes for separating liquids from colloids and in hyperfiltration methods of removing solute from solutions. It provides a method of removing liquid from solids without producing a thick bed of solids on the filtering medium.

In hyperfiltration methods wherein solute-rejecting membranes are dynamically formed i.e. formed in the sense that the membrane is formed as the feed solution containing the membrane-forming material passes over the deposited bed of filter and material, the method of the present invention permits the use of materials as substrates which previously could not be used because of large

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or nonuniform pores.

The thin bed of fine particles functions as a finely pored body and unexpectedly remains uniformly distributed on the substrate even in the presence of high cross flow velocity and tubulent fluid flow (velocities parallel to the bed of 10-20 feet per second are frequently desirable) necessary to prevent fouling of membranes. The flow rate will ordinarily be greater than 1 foot per second and may reach 100 feet per second. Turbulence promoters may be used to minimize fouling if desired. Fouled membranes can also be removed by backwashing and are easily reestablished by providing a new supply of particulates and membrane-forming materials in feed solutions.

As used herein, the term "porous substrate" refers to the coherent permeable base material onto which a thin bed of fine inert particles is deposited. The term "porous support" refers to the combination of a porous substrate and a bed of fine particles onto which a rejecting membrane may be deposited for hyperfiltration methods of removing solute from solution, and "filtering medium" refers to the composite used for filtering, including a rejecting membrane in the case of hyperfiltration processes.

The method of the present invention differs from prior filtration methods using filter aids in that our method combines a high cross flow rate with the filter aid and requires only relatively small quantities of the filter aid.

### *Description of the Preferred Embodiments*

In carrying out the process of the present invention a thin bed of fine particles is deposited onto a porous substrate. The substrate may be of any material compatible with solutions to be in contact with it and may be of any configuration. While our method may be used with a substrate having small uniform pores, its primary advantages are with a substrate having large or nonuiform pores. It is most useful with substrates having pores whose average diameter exceeds 5 microns and the preferred pore range is 5 to 50 microns in diameter. It is possible to use flexible and woven materials including porous, pressure-resistant tubes, as well as rigid substrates such as porous metals, ceramics and carbons.

The particles deposited on the substrate surface may be of any material inert to the solutions to be in contact with them, and materials available as filter aids such as diatomaceous earth, perlite, asbestos fibers, cellulose fibers, dried silica gel, and carbon may be used. The particle shape is not critical and it may be spherical, fibrous, or irregular. The average particle diameter is between 0.01 and 100 microns and is determined by factors such as the pore size of the substrate and the nature of the material to be filtered.

The thin bed may be essentially a monolayer of particles or it may be a multilayered structure. In some instances, as where a large-pored substrate is to be used to separate a liquid from submicron-size particles, several layers of different-size particles may be desirable. The thickness of the bed is between 0.1 and 100 microns and will normally be controlled by the cross flow rate.

The particles may be deposited on the substrate by passing a dilute slurry (one to several thousand parts per million) of particles over the substrate under conditions where there is a pressure drop across the substrate wall. A thin layer of particles will deposit and remain on the substrate surface even at a high cross flow rate, e.g., a flow of 10-20 feet per second parallel to the substrate surface.

The substrate, together with its coating of fine particles, may be used in hyperfiltration processes, as well as more conventional filtration methods. However, it does not reject solute, but forms a porous support on which a solute-rejecting membrane may be formed by contacting it with a solute-rejecting additive. Examples of substances which may be used as solute-rejecting additives are neutral organic polymers, polyelectrolytes, organic ion exchangers, inorganic ion exchangers, and hydrous metal oxides.

The method of the present invention is useful in forming porous supports for hyperfiltration methods of removing organic solute as well as inorganic solute from solutions.

Having thus described the invention ,the following examples are offered to illustrate it in more detail.

### *EXAMPLE 1*

In a laboratory hyperfiltration apparatus, three tubes were connected in parallel with means for supplying pressurized feed on their respective outsides and means for collecting the liquid passing through the tube walls. The first tube, made from a compact of spherical mineral particles, had an average pore diameter of 30 microns; the second tube was made of porous stainless steel and had a nominal pore diameter of 5 microns; and the third tube was made of a ceramic and had a nominal pore diameter of 50 microns. A slurry containing 0.02 per cent by weight of a diatomite filter aid having an average particle diameter of 5.4 microns was pumped past the tube walls, thereby depositing a layer of particles sev-

eral microns thick on the tube surfaces. This layer did not reject the salt when a solution of 0.025 molar of $MgCl_2$ in water was pumped over the surface at a pressure of 150 psi. A solution containing hydrous Zr(IV) oxide to form a rejecting membrane was then added to the $MgCl_3$ solution. The degree of $MgCl_2$ rejection and the permeation rate of the tubes in gallons per day per square foot (gpd5ft²) were measured. The data as to permeation rate and rejecting values are given in Table I below.

*TABLE I*

*Rejection of $MgCl^2$ by Hydrous Zr (IV) Oxide Membrane*

| *Tube Type* | *Permeation Rate, gpd/ft²* | *Rejection, per cent* |
|---|---|---|
| Compacted mineral particles | 140 | 70 |
| Stainless steel | 100 | 55 |
| Ceramic | 250 | 70 |

As seen from this example, a rejecting membrane having high flow rates and excellent rejection capability can be formed on large-pored material with our method.

*EXAMPLE II*

Three ceramic tubes having nominal pore diameters of 20 microns, 1.4 microns, and 0.6 micron were connected in parallel as in Example I. An aqueous phase containing 50 to 150 parts per million of a diatomite filter aid having a median particle diameter of 5.4 microns was forced over the outside surfaces of the tubes and some liquid withdrawn from their interiors. A layer of filter aid particles several microns thick was deposited on the tubes by this technique.

A feed material comprising a solution obtained from a sewage plant after primary treatment was then passed over the resulting tubes. Constituents present in the primary sewage effluent formed a membrane which rejected organic materials. The rejection of chemical oxygen demand for the first tube was between 50 and 70 per cent and for the second and third tubes was 90 per cent at a transmission rate of 50 to 100 gpd/ft².

The foregoing example illustrates the formation of a membrane capable of rejecting organic materials on our porous support.

*EXAMPLE III*

A stainless steel tube having a nominal pore diameter of 5 microns and a tube made from a compact of spherical mineral particles having a nominal pore diameter greater than 30 microns were coated with a diatomite filter aid having a median particle diameter of 5.4 microns by forcing an aqueous slurry containing 100 ppm of the filter aid over the outer surfaces of the tubes and withdrawing some liquid from their interiors. A feed solution consisting of wash liquors from a sulfite pumping process and a solute-rejecting material was then forced past the outer surface of the tubes at a velocity of 3 to 6 feet per second. The rejection of dissolved matter absorbing light having a wave length of 2810 Å was up to 90 per cent at permeation rates of 25 to 90 gpd/ft² for the tube with 30-micron pores and over 80 per cent for the tube having 5-micron pores at permeation rates of 10 and 100 gpd/ft².

Example III illustrates the use of the process of the present invention in treating a typical pollution control problem.

Example IV is given to illustrate the use of a backwashing technique with out invention.

*EXAMPLE IV*

In a series of five tests with salt-rejecting membranes dynamically formed of mixed poly(vinyl pyridine) and poly(vinyl pyrrolidone) on a perlite filter aid layer supported on a porous stainless steel tube with 10-micron-diameter pores, the tubes were backwashed with water at a few hundred psi between the experiments. The permeabilities of the tubes after backwashing were within 30 per cent of the original value, while the permeabilities of the tubes with pre-deposited membranes, i.e. membranes which are formed prior to passing the feed solution across the bed of filter and material, were a hundred to a thousand times lower. This demonstrates that backflushing can be used to restore permeability if it slows to unacceptably low values because of fouling or other reasons, or a new membrane can be deposited in the event requirements change, e.g., a need to filter a different solute.

*EXAMPLE V*

A dynamic salt-rejecting membrane was developed on a section of a fire hose jacket with outside diameter 1.28 inches. The hose was made of cotton with warp yarn 8/7, warp ends 126, filler yarn 8/22, filler picks 10.5/in. A section of this hose was clamped in a hyperfiltration apparatus. It was then coated on the inside by passing through it an aqueous suspension of various grades of a diatomaceous earth filter aid. The deposition was carried out at an axial flow rate (cross flow velocity) of 3.3 feet/second. Three grades of filter aid were used in succession. The median particle diameter of the first grade was 30 microns; that of the second grade was 20 microns; and that of

the third grade was 10 microns. The concentration of filter aid in the suspension was approximately 40 mg/liter.

After preparing this porous multi-layered support, a 0.02 molar $MgCl^2$ solution was circulated which contained $4 \times 10^{-4}$ molar hydrous zirconium (IV) oxide prepared by hydrolysis of zirconium oxychloride. Within 16 hours salt rejection was 62 per cent and after approximately 40 hours salt rejection was found to be over 80 per cent at an axial circulation velocity of 16 ft/sec. Flow through the filtering medium was 0.45 cm/min (160 gpd/ft$^2$) at 200 psi applied pressure.

This example illustrates the use of woven materials as porous substrates in combination with filter aids and dynamic membranes for rejection of dissolved materials. It is clear that other hose materials could be used such as those prepared from synthetic fibers, glass fibers, with the only restriction being that the fibers not be attacked by the solutions with which they come in contact. Also, other types of weaves capable of retaining the filter aid would be satisfactory.

WHAT WE CLAIM IS:—

1. A process for removing extraneous materials which are dissolved in an aqueous feed solution which comprises depositing, to a depth of from 0.1 to 100 microns, a bed of particles of an inert filter aid material on the internal or external surface of a porous tubular substrate, said particles having a size in the range of 0.01 to 100 microns, incorporating a solute-rejecting material in said feed solution if not originally present therein, and passing said feed solution across the deposited bed while maintaining a velocity parallel to the bed sufficient to prevent fouling of the solute-rejecting membrane formed thereon from said solute-rejecting material, and a pressure across said bed sufficient to cause an aqueous solution to issue from the non-deposited surface of said substrate which solution is depleted in extraneous materials.

2. A process as claimed in claim 1 in which the inert filter aid material is slected from diatomaceous earth, perlite, asbestos fibres, cellulose fibres, dried silica gel or carbon.

3. A process as claimed in claim 1 or 2 in which the pores of said porous tubular substrate have an average diameter greater than 5 microns.

4. A process as claimed in any preceding claim in which said feed solution is passed across the deposited bed at a cross flow velocity of between 1 and 100 feet per second.

5. A process as claimed in any preceding claim in which the deposited bed comprises a multi-layered deposit.

6. A process for removing extraneous materials which are dissolved in an aqueous feed solution as claimed in claim 1 substntially as hereinbefore described.

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